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DESIGN OF A THREE-LAYER ANTIREFLECTION COATING FOR HIGH EFFICIENCY INDIUM PHOSPHIDE SOLAR CELLS USING A CHEMICAL OXIDE AS FIRST LAYER

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ABSTRACT

It is well known that the behavior of III-V compound based solar cells is largely controlled by their surface, since the majority of light generated carriers (63% for GaAs and 79% for InP) are created within 0.2 μm of the illuminated surface of the cell. Consequently, the always observed high surface recombination velocity (SRV) on these cells is a serious limiting factor for their high efficiency performance, especially for those with the p-n junction made by either thermal diffusion or ion implantation. A good surface passivation layer, ideally, a grown oxide as opposed to a deposited one, will cause a significant reduction in the SRV without adding interface problems, thus improving the performance of III-V compound based solar cells. Another significant benefit to the overall performance of the solar cells can be achieved by a substantial reduction of their large surface optical reflection by the use of a well designed antireflection (AR) coating.

In this paper, we demonstrate the effectiveness of using a chemically grown, thermally and chemically stable oxide, not only for surface passivation but also as an integral part of a 3-layer AR coating for thermally diffused p^+n InP solar cells. A phosphorus-rich interfacial oxide, $\text{In}(\text{PO}_3)_3$, is grown at the surface of the p^+ emitter using an etchant based on HNO_3 , $\text{o-H}_3\text{PO}_4$ and H_2O_2 . This oxide has the unique properties of passivating the surface as well as serving as a fairly efficient antireflective layer yielding a measured record high AM0, 25°C, open-circuit voltage of 890.3 mV on a thermally diffused InP(Cd,S) solar cell. Unlike conventional single layer AR coatings such as ZnS, Sb_2O_3 , SiO or double layer AR coatings such as ZnS/MgF₂ deposited by e-beam or resistive evaporation, this oxide preserves the stoichiometry of the InP surface. We show that it is possible to design a three-layer AR coating for a thermally diffused InP solar cell using the $\text{In}(\text{PO}_3)_3$ grown oxide as the first layer and Al_2O_3 , MgF₂ or ZnS, MgF₂ as the second and third layers respectively, so as to yield an overall theoretical reflectance of less than 2%.

Since chemical oxides are readily grown on III-V semiconductor materials, the technique of using the grown oxide layer to both passivate the surface as well as serve as the first of a multilayer AR coating, should work well for essentially all III-V compound-based solar cells.

INTRODUCTION

Calculations show that the majority of light generated carriers in direct bandgap III-V compound semiconductor based solar cells, are created within 0.2 μm of the illuminated surface of the cell⁽¹⁾. For such materials, surface recombination velocity (SRV) and p/n junction depth

considerations are of critical importance in the design of high efficiency solar cells. Even though published values of SRV on InP and GaAs vary over a wide range, depending on the surface preparation and the techniques used for measurement⁽²⁾, it is estimated that SRV values can be as high as 1.8×10^7 cm/s^(3,4), even for epitaxially grown cells. Therefore, thin emitters and reduced SRV appear to be necessary conditions for the fabrication of high efficiency III-V compound based solar cells. A good surface passivation layer, ideally a grown oxide, will cause a significant reduction of the SRV without adding semiconductor/oxide interface traps and oxide bulk defects which are inherent to deposited oxides, thus improving the overall performance of the III-V compound based solar cell. Yet another obvious but not often properly addressed limitation to high performance of these cells, is their high surface reflection, particularly in the blue region of the solar spectrum.

In this work, we address these two problems with a new optimized three-layer AR coating for the p^+n InP(Cd,S) thermally diffused solar cell. A chemical oxide grown on the p^+ -doped emitter serves as the first layer of a three-layer AR coating composed of $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$. This $\text{In}(\text{PO}_3)_3$ oxide, which is described in detail elsewhere⁽³⁾, is primarily designed as a surface passivating layer, and has yielded a record high AM0, 25°C open circuit voltage V_{OC} of 890.3 mV, measured on a thermally diffused p^+n InP(Cd,S) solar cell⁽⁵⁾. We also investigate a three-layer AR coating composed of $\text{In}(\text{PO}_3)_3/\text{ZnS}/\text{MgF}_2$. Even though, in this paper, we demonstrate the effectiveness of the above described AR coatings on p^+n InP solar cells, the concept of using a native oxide passivating layer as the first layer of a multilayer AR coating should benefit any III-V compound semiconductor based solar cells, since chemical oxides are readily grown on most III-V semiconductor materials.

EXPERIMENTAL

The 0.8 cm x 0.6 cm p^+n InP solar cells were fabricated using the closed ampoule technique to diffuse Cd into n-InP:S ($N_D - N_A = 3.5 \times 10^{16}$ to 3.1×10^{17} cm⁻³) with Cd_3P_2 as the diffusion source. Diffusion temperatures were from 560° to 660 °C. The substrates were Czochralski (LEC) grown with EPD of about $5\text{-}7 \times 10^4$ cm⁻². Diffusions were performed through chemically grown P-rich oxide cap layers.

Au-Ge was used for the back contact. The Au-Zn (0.18 to 0.3 μm thick) front contact grid was deposited by evaporation and defined using existing photolithography masks, designed for the n/p cell configuration. Because Au based contacts are known to penetrate into InP during sintering at 430 °C, up to depths which are over three times the initial thickness of the evaporated Au-Zn-Au layer, the thickness of the emitter was kept at quite a high value (>3.5 μm) while keeping the thickness of the evaporated contacts below 0.3 μm. After sintering, the thick emitter was thinned down over the uncontacted area using a chemical etch which we call the PNP etch, based on HNO_3 , o- H_3PO_4 , and H_2O_2 , especially developed for this purpose⁽⁶⁾.

The thermal diffusion process just described is inherently a substantially lower cost process as compared to the epitaxial process of junction formation and can potentially be used for large scale batch production of solar cells. To minimize the surface damage which ordinarily always occurs during thermal diffusion, we used a 3 to 5 nm thick $\text{In}(\text{PO}_3)_3$ -rich oxide cap layer in our diffusion process. In addition, we further improved the quality of our diffused surface by doing a chemical treatment with the PNP etchant after sintering the front contacts of the cell. Simple chemical treatments of InP surfaces using HNO_3 and HF based etchants were found to decrease the SRV to below 5×10^5 cm/s, e.g. 1.7×10^5 for n^+ -InP and 4.7×10^5 cm/s for p^+ -InP, after rinsing the substrates in a HNO_3 (15%) solution⁽⁴⁾.

Using the PNP etch, from low frequency EG-V measurements, we recorded a surface state density minimum (N_{SS}) at the Cd-diffused p^+ -InP/passivating layer interface as low as 2

$\times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ (7). About 40 nm was removed from the surface of a the p^+n InP structure diffused at 660 °C (surface acceptor concentration: $\sim 4 \times 10^{18} \text{ cm}^{-3}$; junction depth: $\sim 3.5 \text{ }\mu\text{m}$).

The first layer of the designed three-layer AR coating is chemically grown in the process of thinning the emitter using the PNP etchant. A more detailed description of the composition of this oxide is published elsewhere(7). Here, we will simply state that the residual chemical oxide is a two-layered oxide composed of a thick In-rich outer layer and a P-rich layer at the interface with the emitter. This interfacial oxide is rich in $\text{In}(\text{PO}_3)_3$ and has a bandgap of $6.8 \pm 0.2 \text{ eV}$ (8). Because the dissolution rate is quite reproducible, a controlled thickness of oxide can be grown to serve as the first layer of the designed three-layer AR coating.

The SiO_2 , Sb_2O_3 , MgF_2 and ZnS layers are all deposited by evaporation techniques.

DESIGN OF THE THREE-LAYER AR COATING

The theoretical design of the three-layer AR coating was conducted using standard optical theory based on the matrix description of each layer of a multilayer system. The optical impedance of each layer is assumed known, in order to reduce the number of unknown parameters in the minimization of the reflectance function, and to maintain the problem within the realistic boundaries of commonly used optical materials. The MATLAB algorithm developed to calculate and optimize the parameters of the AR coating is based on work done by Nagendra, and Thutupalli (1988)(9).

For solar cell applications, the design of a good AR coating, contrary to common practice, should not be based merely on reducing the light reflectance but rather maximizing the external quantum efficiency or minimizing the loss of short circuit current due to reflection. This last criterion, expressed in terms of the integrated current loss, defined as the ratio of the integrated short circuit current of the cell to the ideal zero-reflectance integrated short-circuit current, allows one to take into account the incident light spectrum, and eventually the presence of a protective transparent cover glass.

Our experiments have shown that the commonly used double-layer AR coating, ZnS/MgF_2 , deposited on p^+n InP solar cell surface leads to a net decrease of the open circuit voltage (V_{oc}) of the cell by as much as 50 mV due to an increase in SRV(7). For that reason, we recommend a three-layer AR coating with $\text{In}(\text{PO}_3)_3$ passivating oxide as the first layer, followed by either ZnS/MgF_2 or $\text{Al}_2\text{O}_3/\text{MgF}_2$. The $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$ is a new optical system we are proposing for the p^+n InP solar cell. Al_2O_3 is known for its stability, its high dielectric constant, and its radiation tolerance (higher than that of commonly used SiO_2). Also, Al_2O_3 has a closed packed hexagonal crystal structure, closer to that of $\text{In}(\text{PO}_3)_3$. We expect Al_2O_3 to be superior to ZnS . MgF_2 is a generally preferred outer layer which refractive index of 1.37 gives a good optical transition to many protective coverglass/adhesive systems(i.e. fused silica/adhesive 1.46/1.43, microsheet/adhesive 1.53/1.43).

RESULTS AND DISCUSSION

Table 1. and Table 2. give optimum designs of three-layer AR coatings using $\text{In}(\text{PO}_3)_3/\text{ZnS}/\text{MgF}_2$ and $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$ for different thicknesses of the first layer $\text{In}(\text{PO}_3)_3$ and a AMO spectrum ranging from 300 nm to 950 nm. The symbols ICL and IRL represent the Integrated Current Loss, and the Integrated Reflection Loss respectively defined as

$$ICL = 1 - \frac{\int_{\lambda_1}^{\lambda_2} J_{sc, R \neq 0}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} J_{sc, R=0}(\lambda) d\lambda} \quad \text{and} \quad IRL = \frac{\int_{\lambda_1}^{\lambda_2} R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} d\lambda}.$$

The results suggest that the $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$ coating gives a lower ICL than $\text{In}(\text{PO}_3)_3/\text{ZnS}/\text{MgF}_2$ mainly because of a lower blue reflectance, as shown in Fig. 1.

Considering the first layer of the AR coating, Fig.2 shows that the two-layered oxide ($\sim 750 \text{ \AA}$) reduces the surface reflectance of an InP solar cell from an average 40% (curve a) on a bare surface with no oxide, to about 20% (curve c). In this particular case, after removing the In-rich outer oxide layer, the reflectance of the remaining thin $\text{In}(\text{PO}_3)_3$ oxide (300 \AA) is about 25% (curve b). In Fig. 3, it can be seen that a thick two-layered oxide $\text{In}_2\text{O}_3(\sim 900 \text{ \AA})/\text{In}(\text{PO}_3)_3(\sim 300 \text{ \AA})$ gives a lower overall reflectance than a single layer of SiO (800 \AA thick). Its blue reflectance is lower than either SiO , Sb_2O_3 (750 \AA thick), or a double layer of ZnS/MgF_2 (not shown here). However, Sb_2O_3 has lower mid-spectrum reflectance. Our experiments show that single layers of SiO , Sb_2O_3 as well as a double layer of ZnS/MgF_2 , even though they reduce the surface reflection, also tend to increase the surface recombination velocity on the emitter of a p^+n InP solar cell, leading to a decrease of the open circuit voltage by as much as 50 mV⁽⁷⁾. Although the reflectance of the double-layer chemical oxide is lower than that of SiO , it is still too high for use as the only layer of an efficient AR coating. Furthermore, the In-rich outer oxide layer is unstable and quite electrically conductive, causing a noticeable drop in the shunt resistance R_{sh} and V_{oc} of the cells. It therefore cannot be used, but should rather be removed so that only the P-rich oxide remains for use as the first of a three-layer AR coating.

Curve d) of Fig. 2 shows the calculated reflectance of a three-layer antireflective coating composed of $\text{In}(\text{PO}_3)_3$ (400 \AA), Al_2O_3 (549 \AA), and MgF_2 (712 \AA). It can be seen that the reflectance is reduced to an average of less than 2% when the three-layer coating is used. As, shown in table 1, the actual loss of current density due to reflection loss, will be less than 1%, when one takes into account the spectral response of the InP solar cell.

In Table 3 are presented measured and predicted performance parameters of p^+n (Cd,S) InP solar cells. Rows 1,3 and 4 of the data refer to thick In-rich chemical oxides ($\sim 900 \text{ \AA}$ to 1500 \AA) over an interfacial P-rich oxide ($\sim 300 \text{ \AA}$ to 400 \AA). The parameters in rows 2 and 5 were measured after removing the In-rich oxide from the surface. The increase in V_{oc} and FF are expected as current leakage occurs through the In-rich oxide outside the mesa etched active area. The increase in FF is a consequence of an increase in R_{sh} when the In-rich oxide is removed. After depositing 850 \AA of SiO over the 400 \AA thick P-rich oxide, the increase in J_{sc} is consistent with a decrease in reflectivity. The last row of table 3. gives an experiment-based projection of the performance of the cell in row 6, using the optimum three-layer AR coating designed, the grid coverage of a newly acquired photolithography mask (5%), and an experimentally achievable improved series resistance of about $0.8 \text{ } \Omega\text{-cm}^2$. The projected J_{sc} and V_{oc} values of 37 mA/cm^2 and 894 mV respectively can be obtained based on the quantum efficiency curve of this cell. A fill factor, and efficiency values of 80% and 19.4% respectively can be achieved on such a cell. It should be pointed out that these values are below the experiment-based projections for our state-of-the-art p^+n InP solar cells where in addition to using the designed 3-layer AR coating, reducing the emitter junction depth to less than $0.3 \text{ } \mu\text{m}$, the specific contact resistance to less than $10^{-3} \text{ } \Omega\text{-cm}$, should make a solar cell of efficiency, $\eta=21.3\%$ achievable⁽⁵⁾.

CONCLUSIONS

The dual problem of surface passivation and antireflection coating design of III-V compound based solar cells have been addressed. We have designed a three-layer optimized AR coating for p^+n InP solar cell, which brings the average reflectance down from about 40% to less than 2% while at the same time significantly improving the J_{SC} and V_{OC} by passivating the top surface of the emitter. This has been accomplished by using a chemically grown $\text{In}(\text{PO}_3)_3$ -rich passivating oxide layer as the first layer of a 3-layer AR coating, with Al_2O_3 and MgF_2 as the second and third layers. We believe that the significant front surface passivation is to a large extent responsible for our achieving the record high efficiency V_{OC} of over 890 mV. This concept of using a passivating chemically grown oxide as the first layer of a multilayer AR coating can be beneficial to other III-V compound solar cells as well.

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Table 1: Summary of 3-layer ARC design with $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$

$d_{\text{In}(\text{PO}_3)_3}$ (Å)	$d_{\text{Al}_2\text{O}_3}$ (Å)	d_{MgF_2} (Å)	J_{sc} (AMO) mA/cm^2	ICL (%)	IRL (%)
50	647	490	43.99	1.62	2.12
100	602	510	44.00	1.60	2.09
150	534	558	44.03	1.54	2.01
200	460	616	44.06	1.46	1.85
250	420	641	44.11	1.37	1.73
300	422	635	44.17	1.23	1.54
350	425	624	44.24	1.06	1.38
400	549	712	44.43	0.64	1.03
450	425	656	44.34	0.83	1.81
500	500	465	44.06	1.48	2.79

Table 2: Summary of 3-layer ARC design with $\text{In}(\text{PO}_3)_3/\text{ZnS}/\text{MgF}_2$

$d_{\text{In}(\text{PO}_3)_3}$ (Å)	d_{ZnS} (Å)	d_{MgF_2} (Å)	J_{sc} (AMO) mA/cm^2	ICL (%)	IRL (%)
50	466	899	44.29	0.95	1.30
100	415	898	44.28	0.97	1.36
150	363	894	44.27	0.99	1.40
200	417	767	43.08	3.66	6.13
250	197	825	43.75	2.15	2.59
300	239	918	44.3	0.93	1.79
350	291	773	43.88	1.88	1.89
400	240	760	43.78	2.10	2.06
450	178	753	43.69	2.29	2.22
500	114	752	43.64	2.41	2.33

Table 3: AM0, 25°C performances of selected p⁺n InP diffused solar cells measured at NASA LeRC.

AR Coating	Approx. Emitter Thickness (μm)	R _s (Ω-cm ²)	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF (%)	η (%)
In ₂ O ₃ (~1500 Å)/In(PO ₃) ₃ (~400 Å)	0.45	3.52	26.3	887.6	69	11.98
In(PO ₃) ₃ (~400 Å)	0.45	3.24	27.5	884.6	73.7	12.95
In ₂ O ₃ (~900 Å)/In(PO ₃) ₃ (~300 Å)	0.4	3.35	28.2	881.7	72.6	13.2
In ₂ O ₃ (~1100 Å)/In(PO ₃) ₃ (~400 Å)	0.3	4.38	29.4	877.2	61.7	11.63
In(PO ₃) ₃ (~400 Å)			27.6	886.6	62.8	11.25
SiO ₂ (~850 Å)/In(PO ₃) ₃ (~400 Å)			30.95	887.5	61.5	12.36
* Optimized In(PO ₃) ₃ (400 Å)/Al ₂ O ₃ (549 Å)/MgF ₂ (712 Å)	0.3	0.8	37.1	894.2	80.1	19.43

Cell area: 0.48 cm²; front coverage: 9.55%; distance between the 0.3 μm thick fingers: 620 μm. * Experiment-based projected parameters for the cell in row 6.

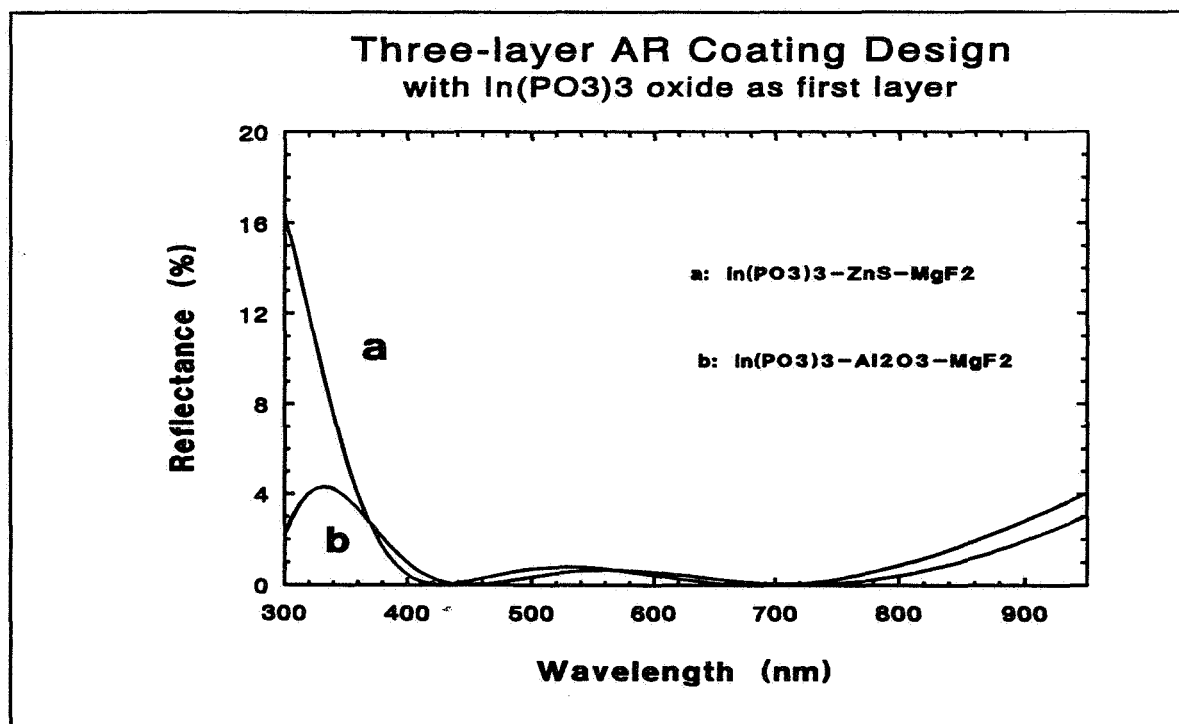


Fig. 1. Reflectance on optimized Three-layer AR coating using: a) In(PO₃)₃/ZnS/MgF₂ b) In(PO₃)₃/Al₂O₃/MgF₂

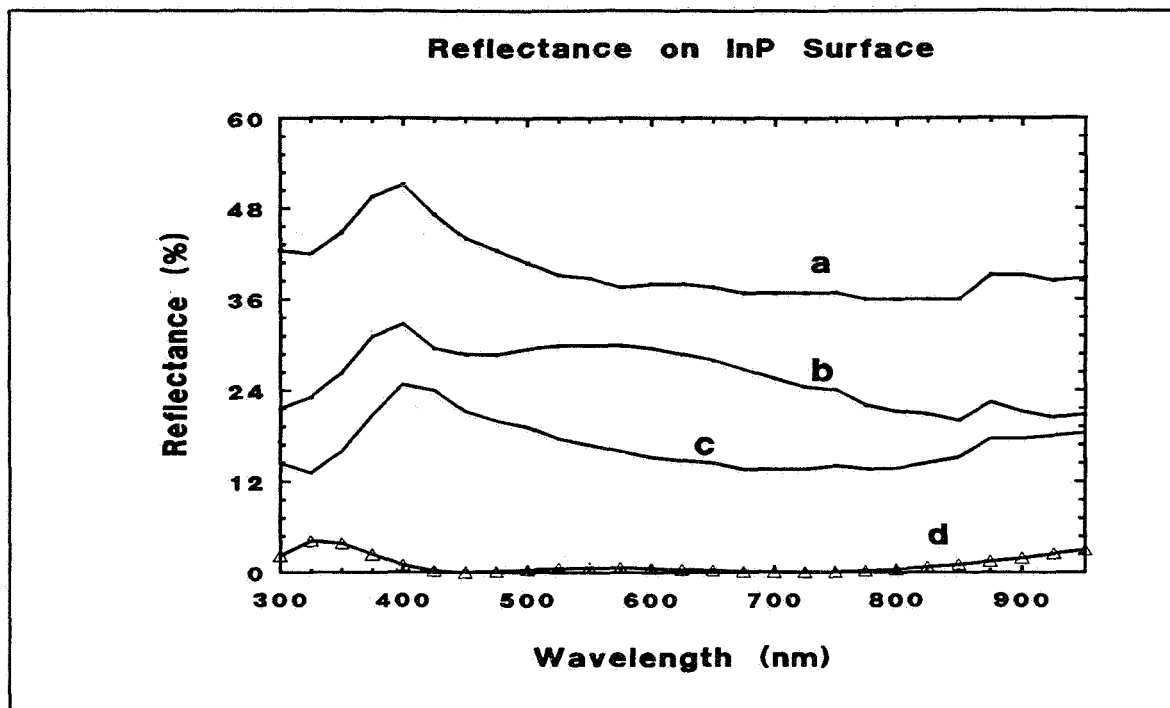


Fig. 2: Surface reflectance vs. wavelength of a) a bare p^+n InP surface (no oxide), no grid fingers; p^+n InP solar cells with: b) 10.5% grid coverage, 400 Å thick surface oxide layer; c) 10.5% grid coverage and 750 Å surface oxide; d) a 3-layer AR coating, $\text{In}(\text{PO}_3)_3/\text{Al}_2\text{O}_3/\text{MgF}_2$.

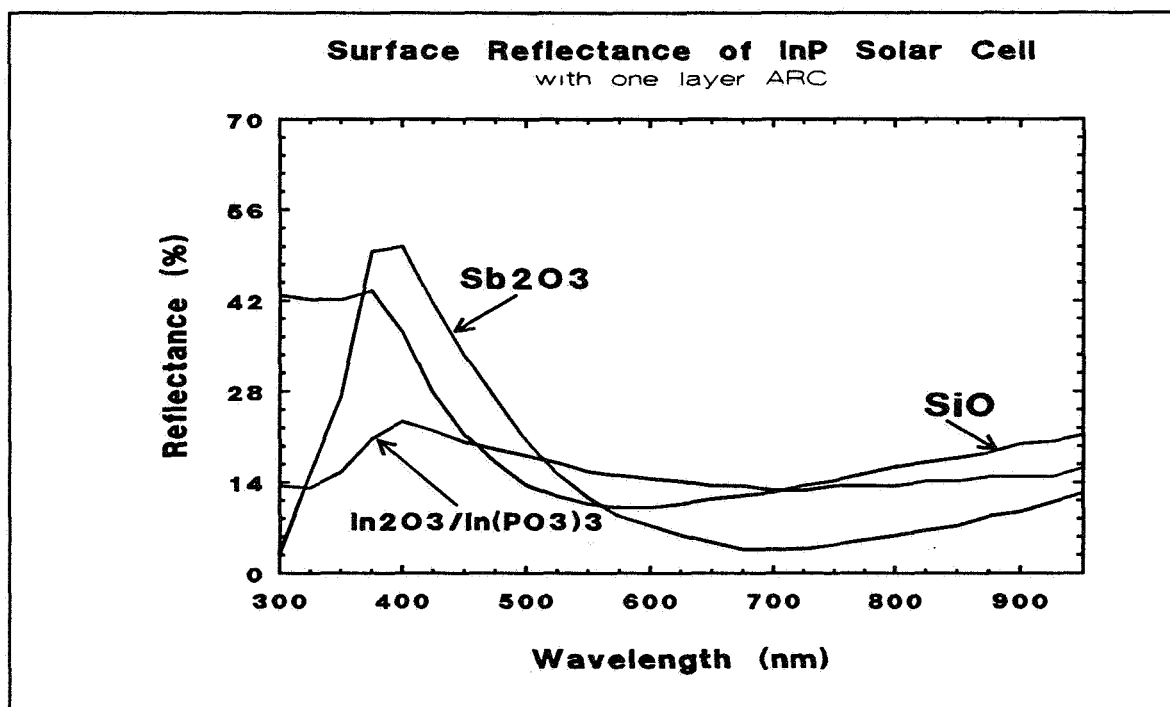


Fig. 3: Surface reflectance vs. wavelength of p^+n InP solar cells using single layer AR coating of the passivating chemical oxide ($\text{In}_2\text{O}_3/\text{In}(\text{PO}_3)_3$ ~1100/400Å); SiO (800Å); and Sb_2O_3 (750Å).